

## ORIGINAL RESEARCH

# Enhancing bioenergy production from food waste by in situ biomethanation: Effect of the hydrogen injection point

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## Abstract

The increasing rate of food waste (FW) generation around the world is a growing environmental concern, notwithstanding, its valorisation through anaerobic digestion (AD) makes it a potential resource. Moreover, there is a growing demand to optimise the biomethane from AD for gas-to-grid (GtG) and vehicular applications. This has spurred researches on hydrogen gas (H<sub>2</sub>) injection into AD systems to enhance the biological conversion of H<sub>2</sub> and carbon dioxide (CO<sub>2</sub>) to methane (CH<sub>4</sub>), a process known as biomethanation. A simplistic approach for biomethanation is to add H<sub>2</sub> directly into working AD reactors (in situ biomethanation). However, a competition for the injected H<sub>2</sub> towards other biological reactions besides H<sub>2</sub>/CO<sub>2</sub> conversion to CH<sub>4</sub> could follow, thus, reducing the efficiency of the system. Hence, this study was conducted to understand how different H<sub>2</sub> injection points would affect H<sub>2</sub>/CO<sub>2</sub> conversion to CH<sub>4</sub> during FW in situ biomethanation, to identify an optimal injection point. Experiments were designed using H<sub>2</sub> equivalent to 5% of the head-space of the AD reactor at three injection points representing different stages of AD: before volatile fatty acids (VFA) accumulation, during VFA accumulation and at depleted VFA intermediates. Lower potential for competitive H<sub>2</sub> consumption before the accumulation of VFA enabled a high H<sub>2</sub>/CO<sub>2</sub> conversion to CH<sub>4</sub>. However, enhanced competition for soluble substrates during VFA accumulation reduced the efficiency of H<sub>2</sub>/CO<sub>2</sub> conversion to CH<sub>4</sub> when H<sub>2</sub> was added at this stage. In general, 12%, 4% and 10% CH<sub>4</sub> increases as well as 39%, 25% and 34% CO<sub>2</sub> removal were obtained for H<sub>2</sub> added before VFA accumulation, during VFA accumulation and at depleted VFA intermediates, respectively. For immediate integration of biomethanation with existing AD facilities, it is suggested that the required H<sub>2</sub> be obtained biologically by dark fermentation.

## KEYWORDS

anaerobic digestion, biological CO<sub>2</sub> conversion, food waste, hydrogen injection point, in situ biomethanation

# 1 | INTRODUCTION

A third of the food crops cultivated annually (about 1.3 billion tonne—Bt) for human consumption is reportedly wasted or lost at some level within the food supply chain from production to consumption (FAO, 2011); accounting for 44% of global waste (Kaza et al., 2018). It is reported that annual global solid waste generation will increase from the 2.01 billion tonnes estimate of 2016 to 2.59 billion tonnes in 2030 and 3.40 billion tonnes in 2050 (Kaza et al., 2018), consequently, FW increases are expected. Although this increasing rate of FW generation around the world is a growing environmental concern, its valorisation through anaerobic AD makes it a potential resource.

Biological upgrade of AD biogas to biomethane (biomethanation) provides more opportunities to fully exploit biogas potentials through GtG applications and use as vehicle fuel. Hence, biomethanation is becoming a highly researched area within the AD community.

Biological enrichment of  $\text{CH}_4$  using anaerobic microorganisms that can convert  $\text{H}_2/\text{CO}_2$  to  $\text{CH}_4$  (also known as biomethanation) is increasingly being explored, to replace the conventional physicochemical technologies. Physicochemical technologies for biogas upgrade separate  $\text{CO}_2$  in the biogas from  $\text{CH}_4$  and includes processes such as absorption, adsorption and cryogenic and membrane separation (Angelidaki et al., 2018). These technologies are associated with a 20%–72% elevation in  $\text{CH}_4$  production cost due to high energy, chemical and water demand, and up to 8%  $\text{CH}_4$  losses (Linville et al., 2016). Also, additional waste is generated from these processes (Ullah Khan et al., 2017) and the regeneration of the adsorbent media releases the entrapped  $\text{CO}_2$  into the atmosphere (Aryal et al., 2018; Linville et al., 2016), thus, reducing the carbon savings from biogas applications (Bright et al., 2011). However, biomethanation has the potential to double the original mass of  $\text{CH}_4$  and can effectively remove  $\text{CO}_2$  from the biogas for use in microbial metabolism, such that the  $\text{CO}_2$  is not released into the atmosphere (Muñoz et al., 2015; Ryckebosch et al., 2011). Additionally, impurities in the biogas such as ammonia, carbon monoxide and hydrogen sulphide ( $\text{H}_2\text{S}$ ) can be harnessed by the microorganisms during  $\text{CH}_4$  enrichment (Aryal et al., 2018).

Typically, biomethanation can be mediated either *ex situ* (supply of  $\text{H}_2$  into an external reactor enriched with hydrogenotrophic methanogens), *in situ* (direct supply of  $\text{H}_2$  into the anaerobic digester treating a feedstock) or a combination of both *ex situ* and *in situ* (hybrid; Angelidaki et al., 2018; Zabranska & Pokorna, 2018). *In situ* biomethanation allows for efficient use of available hydrogenotrophic methanogens and volumetric space, thus, eliminating the extra cost for a post AD biogas treatment infrastructure (Aryal et al., 2018).

Low gas–liquid  $\text{H}_2$  mass transfer due to its low solubility (15.5 mg/L at 25°C) is a common limitation to biomethanation (Angelidaki et al., 2018). In this regard, academic researches have increasingly focused on process modifications to improve gas–liquid  $\text{H}_2$  mass transfer including, the mixing regime (Luo & Angelidaki, 2012; Yun et al., 2017), packing materials such as alumina ceramic sponge and rushing rings (Bassani et al., 2016) and the  $\text{H}_2$  injection approach.  $\text{H}_2$  injection approaches include pulse injections (Agneessens et al., 2017; Wahid et al., 2019), trickling filters (Rachbauer et al., 2016), hollow fibre membranes (Alfaro et al., 2019; Luo & Angelidaki, 2013a) and ceramic and column diffusers (Luo & Angelidaki, 2013b). While these processes have recorded significant  $\text{CH}_4$  enrichment (up to 100%), the efficiency of  $\text{H}_2/\text{CO}_2$  conversion for *in situ* biomethanation as influenced by the digestion stages (according to the VFA regime) during which  $\text{H}_2$  is injected has not been studied.

AD progresses by the complex interaction of microorganisms according to four stages: hydrolysis, acidogenesis (primary fermentation), acetogenesis (secondary fermentation) and methanogenesis (hydrogenotrophic and acetoclastic), which have different reactions to a surge in  $\text{H}_2$  and potentials for a competitive  $\text{H}_2$  consumption (Kumaran et al., 2016; Schink et al., 2017). By implication, the reactive stage during which  $\text{H}_2$  is injected will affect the rate of  $\text{H}_2/\text{CO}_2$  conversion to  $\text{CH}_4$ . A competition for the added  $\text{H}_2$  by other  $\text{H}_2$  consumers could occur, through other  $\text{H}_2$  sinks, such as acetate production by homoacetogenesis and sulphides production (sulphidogenesis), leading to low  $\text{H}_2/\text{CO}_2$  to  $\text{CH}_4$  conversion efficiency.

According to the AD process thermodynamics,  $\text{H}_2$  utilisation would follow the order: sulphidogenesis > hydrogenotrophic methanogenesis > homoacetogenesis. The metabolism of each process, however, would depend on some factors including, the degraded state of the substrate; availability of combining elements such as  $\text{CO}_2$  for hydrogenotrophic methanogens and homoacetogens and sulphur/sulphate for sulphate-reducing bacteria (SRB); the presence of inhibitors (including  $\text{H}_2$ ) and operating conditions like pH (Chen et al., 2014). Hence, considering the underlying complexities associated with  $\text{H}_2$  production, storage and transportation, it is important to optimise the process such that most (if not all) of the  $\text{H}_2$  used for *in situ* biomethanation is efficiently utilised for  $\text{CO}_2$  conversion to  $\text{CH}_4$ .

Biomethanation have been highly researched using low-organic substrates such as cattle manure, sewage sludge and glucose. Researches on biomethanation using FW are relatively under-developed, limited to recent studies (Okoro-Shekwaga et al., 2019; Tao et al., 2020; Yang et al., 2020). Moreover, Okoro-Shekwaga et al. (2019), suggested that FW was a suitable substrate for *in situ* biomethanation due to a high potential for volatile fatty acids (VFA)-induced pH buffer. The authors reported that using FW, pH levels

were maintained within an optimal pH range of 6.8 to 7.4 (Kumaran et al., 2016).

The highly organic and heterogeneous characteristic of FW makes it behave differently from other typical substrates during AD. Therefore, it can be expected to behave differently with biomethanation, so that, findings from biomethanation studies on other typical substrates might not be directly applicable to FW. Also, high-organic substrates, such as food and green waste, are on a global increase and thus, hold great potential as a resource for in situ biomethanation in the future. In the United Kingdom (UK), for instance, FW remains the largest AD feedstock (asides from other liquid feedstock such as sewage sludge), with about 22.9% of the FW generated annually processed through AD (WRAP, 2015).

Therefore, this study explores FW in situ biomethanation, with H<sub>2</sub> injection at different AD stages; analysing its stability and the possibility of a competitive H<sub>2</sub> utilisation for other processes besides biomethane production. Three H<sub>2</sub> injection points were selected, which correspond to periods before VFA accumulation (hydrolysis), during VFA accumulation (fermentation) and with depleted VFA intermediates. The findings from this study posit that FW in situ biomethanation has a great potential to become the game-changer modification aimed at enhancing biological CO<sub>2</sub> capture and valorisation for the production of bio-based renewable energy from FW.

## 2 | METHODOLOGY

### 2.1 | Food waste characterisation

Waste samples were collected from the University of Leeds' student refectory for 5 days in separately monitored bins. FW sorting, storage and characterisation method follow the methods described in a previous study (Okoro-Shekwaga et al., 2020). The characteristics of the FW used in this study are presented in Table 1, which includes pH, total solids (TS), volatile solids (VS), total chemical oxygen demand (TCOD) and total VFA (TVFA). FW samples were diluted by pre-determined factors before some analyses, including 1 in 5 ml dilution for pH and VFA and 1 in 1000 ml dilution for COD. The final COD and VFA results were corrected by the respective dilution factors, while pH was reported without conversion. The analytical methods employed are described in Section 2.4.2.

### 2.2 | Inoculum preparation

Digestate collected from an anaerobic digester fed with sewage sludge at mesophilic temperature was used as inoculum. The inoculum was collected from Yorkshire Water's Esholt

TABLE 1 Characteristics of FW used in this study and the reactor content (liquid phase) before H<sub>2</sub> addition

	Food waste used	Exp1			Exp2			Exp3		
		Blank	Control	Test	Blank	Control	Test	Blank	Control	Test
pH	4.8 (0.0)	8.6 (0.0)	8.5 (0.0)	8.5 (0.0)	7.7 (0.0)	7.1 (0.0)	7.0 (0.0)	8.2 (0.0)	7.0 (0.0)	7.0 (0.0)
TS (g/L)	314.3 (0.2) <sup>a</sup>	10.5 (0.3)	14.3 (0.2)	14.3 (0.2)	10.3 (0.3)	11.6 (0.2)	11.6 (0.2)	9.8 (0.0)	10.3 (0.0)	10.3 (0.0)
VS (g/L)	295.0 (0.3) <sup>a</sup>	6.1 (0.3)	9.0 (0.2)	9.2 (0.2)	6.0 (0.10)	6.9 (0.1)	6.9 (0.1)	6.3 (0.2)	7.2 (0.1)	7.2 (0.1)
TVFA (mg/L)	5111 (354) <sup>a</sup>	32.6 (4.6)	52.1 (11.3)	52.1 (11.3)	8.9 (2.0)	626.5 (3.5)	626.5 (3.5)	5.1 (1.4)	35.6 (2.5)	35.6 (2.5)
sCOD (g/L)	–	1.2 (0.1)	2.0 (0.1)	2.0 (0.1)	1.3 (0.1)	2.1 (0.1)	2.1 (0.1)	0.7 (0.0)	0.8 (0.0)	0.8 (0.0)
TCOD (g/kg)	469.7 (0.0)	–	–	–	–	–	–	–	–	–

Values in brackets are the corresponding standard deviations from triplicate samples.

<sup>a</sup>TS and VS reported as g/kg and TVFA reported as mg/kg.

Waste Water Treatment Work (Bradford, UK). It was then processed and adapted to FW as described in a previous study (Okoro-Shekwaga et al., 2019).

## 2.3 | Experimental set-up

Wheaton bottles (160 ml) were used as batch anaerobic reactors with 75 ml working volumes and held in a water bath to maintain reactor temperature at 37°C. An inoculum-to-substrate ratio (ISR) of 3:1 based on VS was adopted according to previous ISR optimisation tests (Okoro-Shekwaga et al., 2020). The experiments were set up to include a blank (inoculum only), control (inoculum and FW without H<sub>2</sub> injection) and test (inoculum and FW with H<sub>2</sub> injection) reactors. Blank reactors were set up to assess biogas contribution from the inoculum. Hence, the biogas yield from the blank was subtracted from the respective biogas yields of the control and test and reported accordingly. The control and test were prepared from the same bulk sample, such that, the only difference between both reactors was the injection of H<sub>2</sub> to the test. Three H<sub>2</sub> injection points were chosen according to VFA regimes during batch FW anaerobic digestion in a previous study (Izumi et al., 2010). The authors reported that VFA accumulation peaked 1–3 days after the start of the experiment and decreased rapidly within 6 days (except for propionate). Therefore, the three injection points chosen were Day 0, Day 3 and Day 6 representing periods before VFA accumulation, during VFA accumulation and depleted VFA intermediates and labelled Exp1, Exp2 and Exp3, respectively. The amount of H<sub>2</sub> used was equivalent to 5% of the head-space of the reactor. A relatively low amount of H<sub>2</sub> was used because this study aims to understand the adjustment of the system to in situ biomethanation using FW AD systems. The blank and control reactors were purged with nitrogen gas (N<sub>2</sub>) for 1 min to obtain anaerobic environment and sealed with rubber stoppers and aluminium crimps. H<sub>2</sub> was added to all test reactors by flushing the reactors with a gas mixture of 5%-H<sub>2</sub>:95-N<sub>2</sub> for 1 min. Exp2 and Exp3 bulk samples of the blank and substrate (FW plus inoculum) were prepared in 1 L Duran bottles, with rubber corks and set up to digest anaerobically up till Day 3 and Day 6, respectively. Afterwards, the generated biogas volume and composition from these reactors were measured at the respective days. The bulk samples were then split into Wheaton reactors, followed by a purge with N<sub>2</sub> for 1 min to regain an anaerobic environment and H<sub>2</sub> addition into the test reactors. Hydrogen addition to the reactors follows the method developed by Okoro-Shekwaga et al. (2019), which included hydrogen leak testing. The assays were prepared as sacrificial samples in triplicates for each analytical point (seven per assay), and the characteristics of each reactor are presented in Table 1.

## 2.4 | Analytical methods

### 2.4.1 | Analysis of head-space gas

The volume of the head-space gas was measured by water displacement, according to previously developed methods by Okoro-Shekwaga et al. (2019). The composition of the head-space gas was measured by gas chromatography (GC – Agilent Technology, 7890A), which uses a thermal conductivity detector (TCD) and a Carboxen 1010 PLOT column with the following dimensions: length 30 m, diameter 0.53 mm and film thickness 30 µm. A detailed description of the oven and detector temperatures, carrier gas, injection methods and calibration is described in Okoro-Shekwaga et al. (2019).

### 2.4.2 | Analysis of liquid samples

Standard analytical methods used for the examination of wastewaters and sludge were employed for liquid sample analysis: TS and VS were measured by the gravimetric method as described in 2540 B and 2540 E of standard methods, respectively, and VFA composition was analysed by gas chromatography (GC) analyser (Agilent Technologies, 7890A) as described in 5660 B of standard methods, COD was analysed by the titrimetric method as described in 5220 C of standard methods (APHA, 2005). Soluble COD (sCOD) was conducted on samples' filtrate, by centrifuging the samples at 2000 rpm (775 g) for 5 min using an Eppendorf Centrifuge and filtering the supernatant through 0.45 µm Whatson filter paper, followed by the standard methods for analysing COD (5220 C). The pH was measured using a pH meter (HACH, 40d) and sulphur content was measured using a Thermo Scientific FLASH2000 Organic Elemental Analyzer on samples oven-dried at 40°C and ground to powder.

## 2.5 | Statistical analysis

Descriptive statistical analysis including normality test, mean and standard deviation was conducted on all experimental data. The data from each assay were first subjected to analysis for statistical significance, using a one-sample *t* test. Where significant differences were observed, an additional test was conducted to eliminate outliers.

## 3 | RESULTS AND DISCUSSION

### 3.1 | Hydrogen utilisation

The biogas composition for the periods H<sub>2</sub> was measured in the head-space of the reactors were analysed; test and



control represent reactors with and without  $H_2$  addition, respectively (Table 2). The low solubility of  $H_2$  in water means that changes in the head-space  $H_2$  would be a consequence of gas–liquid  $H_2$  transfers mediated by active microorganisms associated with  $H_2$  consumption or production. The head-space of the control in Exp1 recorded some  $H_2$  up to 48 h after set-up, indicating the production of  $H_2$  for which the rate of consumption was lower than the rate of production and the excess  $H_2$  was transferred to the head-space. Assuming similar  $H_2$  production in the test, then, in addition to the  $H_2$  injected, 4.6 mg- $H_2$ /L would have been expected in the biogas of the test after 24 h. Instead, the head-space  $H_2$  was lower than the external  $H_2$  added by 0.3 mg- $H_2$ /L. For the same period, biomethane concentration in the test was higher than the control by 7.8%, while  $CO_2$  concentration was lower by 1.7%.

The difference in the  $H_2$  of the test between 0 and 48 h was 3.0 mg- $H_2$ /L, which should yield 6.0 mg- $CH_4$ /L, using a stoichiometric  $CH_4$ : $H_2$  mass ratio of 1.99 (Okoro-Shekwaga et al., 2019). Adding this value to the biomethane concentration from the control within 48 h, 27.7 mg- $CH_4$ /L would be expected, which was similar to the actual concentration measured (27.8 mg- $CH_4$ /L). Furthermore, comparing the yields of the test and control between 24 and 48 h, biomethane concentration was higher by 26.9%, while  $CO_2$  concentration was lower by 10.4% in the test. This follows an  $H_2$  utilisation of 2.7 and 0.2 mg- $H_2$ /L in the test and control, respectively, thus, implying enhanced biomethanation in the test as AD progressed, which would also suggest that the  $H_2$  added in Exp1 was mostly utilised for  $CH_4$  production.

A recent study revealed that despite excess  $H_2$  loading, uptake of  $H_2$  by fermenting microorganisms will only be to a very small fraction considering  $H_2$  penetration from saturation into an active methanogenic substrate is less than 1 mm (Aryal et al., 2018). Also, the utilisation of  $H_2$  for sulphate reduction mainly depends on intermediates from anaerobic fermentation/hydrolysis (Hao et al., 2014)—See Section 3.3,

which means  $H_2$  added in Exp1 was primarily utilised towards  $H_2$ / $CO_2$  conversion to biomethane in the test.

In Exp2,  $H_2$  was neither measured in the test nor the control reactors by the next day after addition, believed to be because of heightened competition for common substrates at the fermentation stage (Schink et al., 2017). From Table 2, if all of the added  $H_2$  was utilised to produce biomethane, then the biomethane concentration in the test would have been higher than the control by 7.9 mg- $CH_4$ /L.

However, the difference between the test and the control was 5.4 mg- $CH_4$ /L; being less by 31%. According to Schink et al. (2017), primary fermenters use up the bulk of the energy available during AD (about −280 kJ per mol-glucose) to ferment compounds such as amino acids to glucose, with the excess electrons released in the form of  $H_2$ . After primary fermentation, however, soluble substrates become available for the vast group of microorganisms actively present. As only a small amount of energy is available for secondary fermenters and the cooperating methanogens and sulphate reducers, extensive competition for available energy (substrates) is enriched during secondary fermentation (Schink et al., 2017), which would explain the rapid  $H_2$  utilisation observed in Exp2. As would be discussed later in Section 3.3, results from the sulphur degradation suggest the utilisation of  $H_2$  for other  $H_2$ -influenced processes, thus, buttressing a high competition for the added  $H_2$  Exp2.

Exp3 demonstrated an ultimate consumption of the added  $H_2$  for  $CO_2$  conversion to biomethane. At the time of  $H_2$  addition in Exp3, only trace amounts of acetate and propionate were remaining in the liquid reactor content (see Section 3.2). Thus, little or no competition was expected due to insufficient co-substrates. After 24 h, only 0.20 mg- $H_2$ /L was measured in the test, suggesting a high  $H_2$  uptake of 94.9%. Similarly, Wahid et al. (2019) reported a rapid  $H_2$  uptake of 93% within 24 h, when  $H_2$  was added on Day 9 of in situ biomethanation with glucose. During in situ biomethanation with 5-day pulse  $H_2$  addition, which was started after Day 6 and sewage sludge

**TABLE 2** Mean concentration of biogas components (at STP) in initial days immediately following  $H_2$  addition ( $n = 3$ )

Experiment	Digestion time (h)	Control (mg/L)			Test (mg/L)		
		$H_2$	$CH_4$	$CO_2$	$H_2$	$CH_4$	$CO_2$
Exp1	0	0.0	0.0	0.0	4.0	0.0	0.0
	24	0.6	11.5	108.6	3.7	12.4	106.8
	48	0.4	21.9	200.7	1.0	27.8	179.8
	72	0.0	37.2	350.2	0.0	41.6	293.0
Exp2	0	0.0	0.0	0.0	4.0	0.0	0.0
	24	0.0	63.1	70.1	0.0	68.6	38.5
Exp3	0	0.0	0.0	0.0	4.0	0.0	0.0
	24	0.0	29.4	49.8	0.2	36.3	0.0
	48	0.0	53.4	69.4	0.0	57.9	35.9

Abbreviation: STP, Standard Temperature (273 K) and Pressure (1 atm).

as substrate, Agneessens et al. (2017) reported a high  $H_2$  uptake immediately after  $H_2$  was added, which was completely consumed within 24 h.

For 3.8 mg- $H_2$ /L consumed within 24 h, the biomethane yield in the test was expected to be higher than the control by 7.5 mg- $CH_4$ /L, to give a biomethane concentration of 36.9 mg- $CH_4$ /L. Instead, 36.3 mg- $CH_4$ /L was measured in the test; being less than the expected yield by only 1.4%, which indicates extensive  $H_2$  uptake for methane production. Also, while the concentration of  $CO_2$  in the control was 49.8 mg/L in 24 h, no  $CO_2$  was measured in the test, to further buttress the assertion that the added  $H_2$  was ultimately utilised for methane production. A comparatively high  $H_2$  in Exp3 might be because at steady-state methane production, hydrogenotrophic methanogens are only starved of  $H_2$  and can increase their metabolism to several orders of magnitudes should the substrates be non-limiting (Aryal et al., 2018).

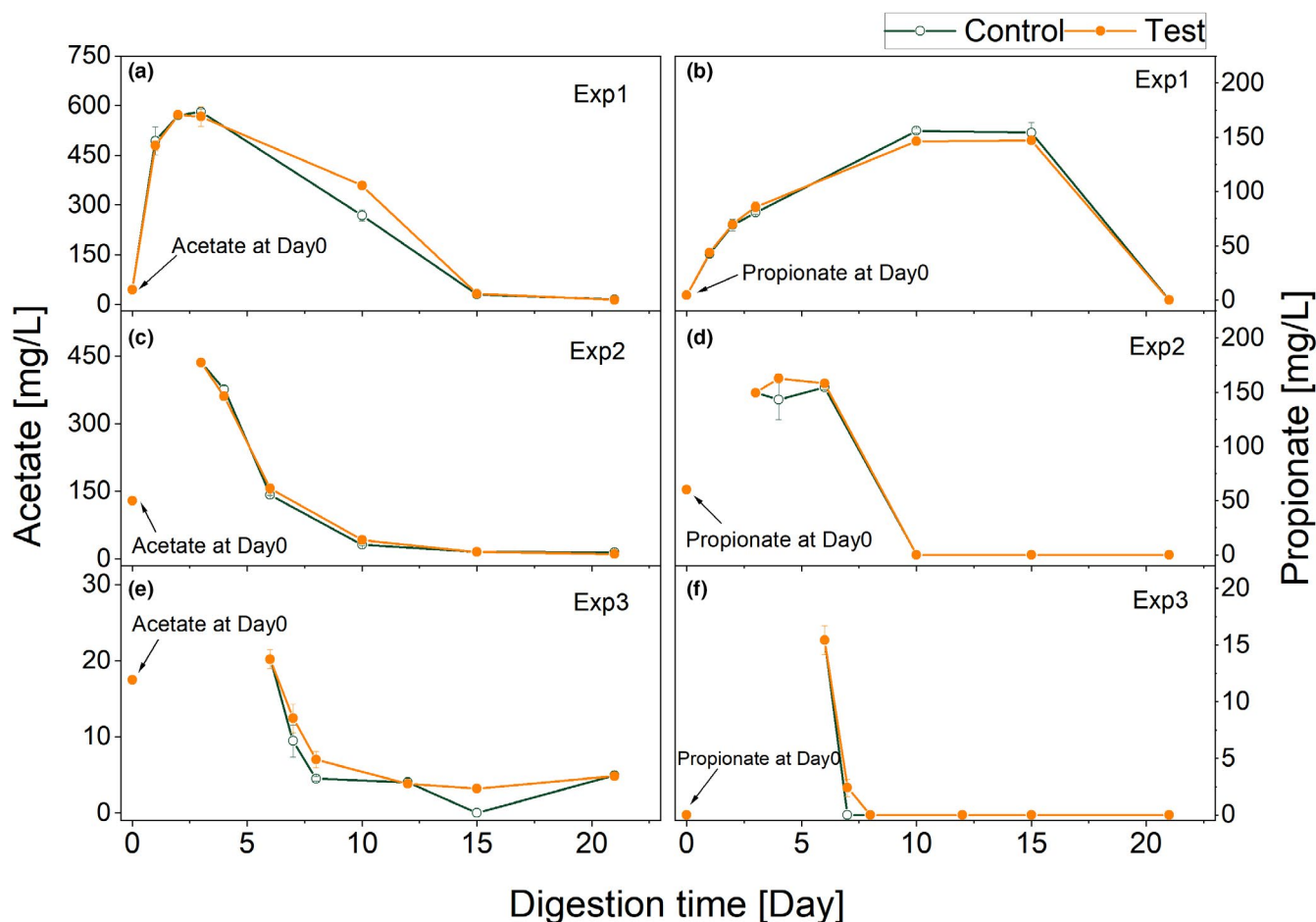
After the complete uptake of the  $H_2$  injected,  $CO_2$  levels were lower than expected in the test of all three experiments. Supposing all the added  $H_2$  were utilised for biomethane production, the  $CO_2$  in the test would be expected to be less by 21.6 mg/L. However, the  $CO_2$  in the test of Exp1, Exp2 and Exp3 was lower than the

corresponding control by 57.2, 31.6 and 33.5 mg/L, respectively. Reportedly, around 0.28%–0.42%  $H_2$  and 3%  $CO_2$  are said to be converted to biomass during biomethanation, such that, the stoichiometric ratio of 4:1 ( $H_2:CO_2$ ) for 1 mole of  $CH_4$  production becomes 4:1.085 (Lecker et al., 2017). Consequently, 6.4%–8.5% losses in  $CO_2$  have been attributed to biomass growth in various biomethanation studies (Burkhardt & Busch, 2013; Lecker et al., 2017; Luo et al., 2012; Rachbauer et al., 2016). As such, the lower than expected levels of  $CO_2$  in the test suggest that methanogenesis was enhanced in all three experiments via the hydrogenotrophic route (Okoro-Shekwa et al., 2019). Exp1 yielded the highest biomethane enrichment, followed by Exp3, suggesting that periods before VFA accumulation and depleted VFA intermediates would support higher conversions.

## 3.2 | Process stability: VFA and pH profiles

### 3.2.1 | Volatile fatty acids profile

During hydrolysis, whereby,  $CO_2$  is the principal inorganic electron acceptor available, the only possible route for  $H_2$



**FIGURE 1** Acetate and propionate levels of the liquid content in Exp1, Exp2 and Exp3: acetate (a, c, e) and propionate (b, d, f). Error bars indicate the standard deviation from the mean

consumption would be by hydrogenotrophic methanogenesis or homoacetogenesis, considering the SRB does not pose a competition at this stage (Chen et al., 2008). Similar acetate levels measured in the control and test for the periods  $H_2$  was measured in the head-space of Exp1 (up to 48 h after the addition—Figure 1a) suggests that the  $H_2$  added to the test was not utilised for homoacetogenesis. The same was observed with propionate profiles of the control and test in Figure 1b. Therefore, Exp1 showed no indication of inhibited VFA degradation for the periods  $H_2$  was measured in the head-space as shown in Figure 1a,b.

In Exp2, whereby complete  $H_2$  uptake was observed within 24 h in the test, acetate level in the test was similar to the control (Figure 1c), while propionate was observed to be 6.9% higher in the test (Figure 1d), suggesting possible inhibition on propionate degradation. This was only to a small extent because of the low levels of  $H_2$  used in this study as well as a concomitant rapid  $H_2$  uptake observed with Exp2. This means if  $H_2$  was added during fermentation at higher concentrations than was used in this study, higher levels of propionate accumulation might occur, consequently, inhibiting acetate and methane production rates (Meng et al., 2013).

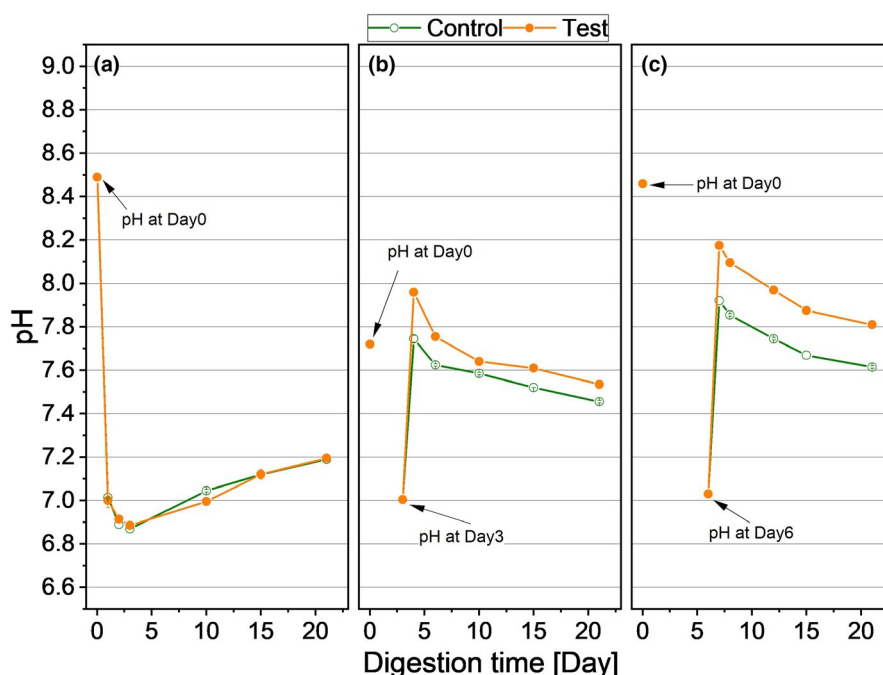
In Exp3, acetate degradation was slower in the test, for the period immediately following  $H_2$  addition, with acetate levels being 31% and 56% higher in the test after 24 and 48 h, respectively (Figure 1e). Perhaps, this was due to an inhibited acetoclastic methanogenesis (Weiland, 2010) or the added  $H_2$  was converted to acetate through homoacetogenesis as a result of the rise in pH (Modestra et al., 2015; see Section 3.2.2). However, acetate may not over-accumulate at this stage of digestion since only a negligible amount of

propionate was available (Figure 1f) and other VFA intermediates were completely depleted.

From all three experiments (Exp1, Exp2 and Exp3), only Exp2 showed signs of VFA (propionate) inhibition, which might be expected to increase in magnitude at higher  $H_2$  loading. Notwithstanding, a rapid utilisation of the added  $H_2$  as observed in Section 3.1 might favour a forward push in propionate degradation, hence, disallowing excessive increases in propionate levels (Meng et al., 2013; Yang et al., 2017). In agreement, when  $H_2$  was added to the co-digestion of manure and acidic whey, Luo and Angelidaki (2013b) reported that acetogenesis was not inhibited. But inhibition to VFA degradation during maize leaf in situ biomethanation was recorded when  $H_2$  was supplied over the stoichiometric  $H_2:CO_2$  ratio (Mulat et al., 2017). During the in situ biomethanation of FW, excessive accumulation of VFA was reported 15 days following the injection of syngas ( $CO/H_2$ —at a ratio of 5/4), which the authors suggested was due to inhibitory effects of CO on the methanogens (Yang et al., 2020). However, with a phased increase in the volume of syngas injected, no VFA accumulation was not observed.

### 3.2.2 | pH profiles

The pH profiles for all three experiments are presented in Figure 2, which shows that the  $H_2$  addition point influenced the extent of pH change of the overall process. The pH of biomethanation systems is often influenced by the  $CO_2$  content of the gaseous phase and the buffering capacity of the liquid phase (Tao et al., 2020). Excessive removal of  $CO_2$  from the AD system causes a rise in pH, which is recommended to be



**FIGURE 2** pH profiles of the liquid content after  $H_2$  addition: (a) Exp1, (b) Exp2 and (c) Exp3. Error bars indicate the standard deviation from the mean

maintained within a range of 6.7 to 7.4 to support optimum methanogenic activities in mesophilic reactors (Wahid et al., 2019). However, the use of acidic substrates helps to buffer down the pH (Luo & Angelidaki, 2013b; Okoro-Shekwaga et al., 2019).

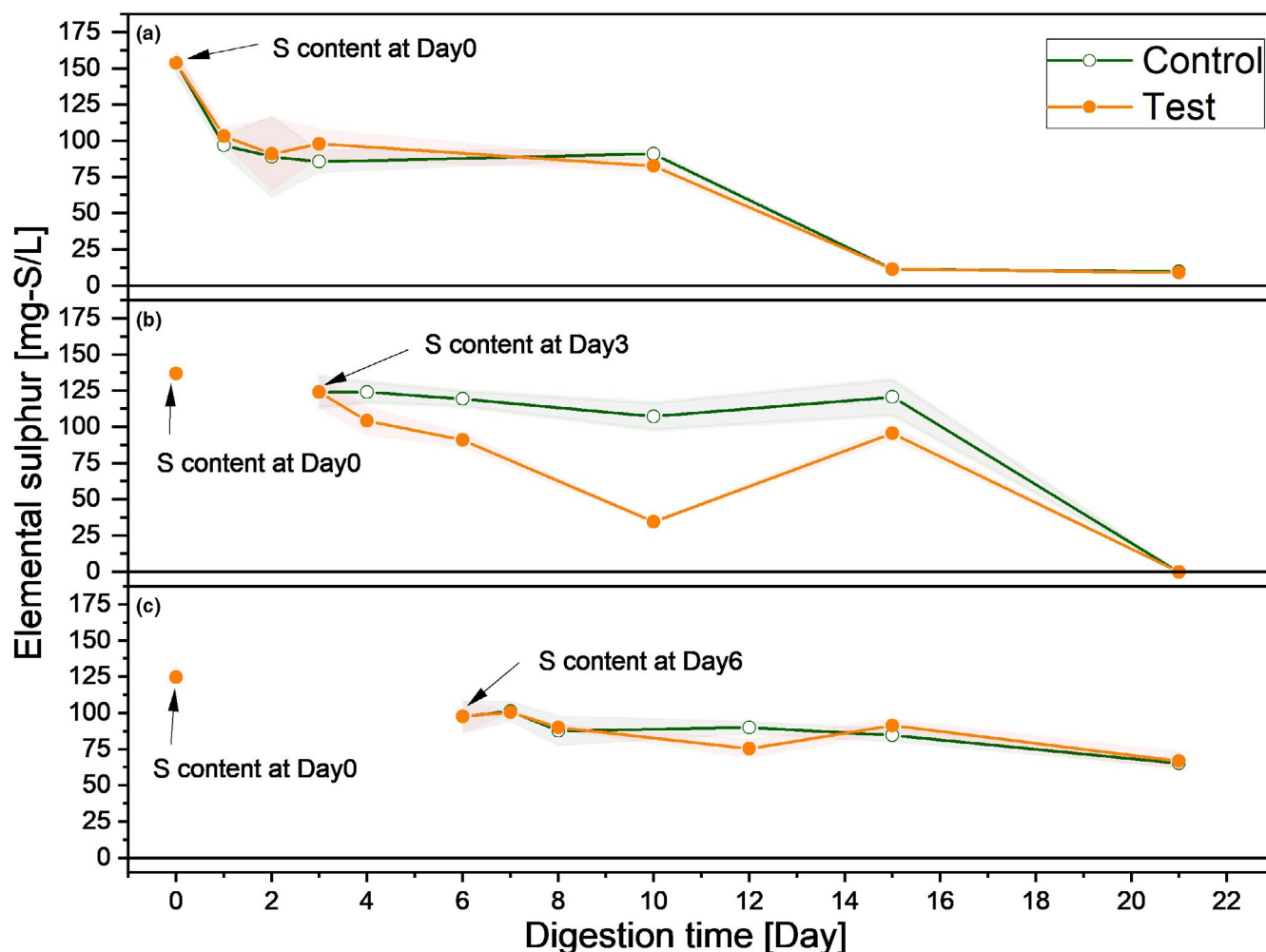
VFA production during primary fermentation caused a decline in the pH of all three experiments immediately after set-up (Kumaran et al., 2016). This high concentration of VFA, which becomes available after  $H_2$  was injected in the test of Exp1, helped to buffer the pH within optimal limits, despite a progressive bimethanation (Okoro-Shekwaga et al., 2019). Thus, the pH of the test in Exp1 remained similar to the control (Figure 2a).

The increase in the pH of the control in Exp2 and Exp3 (Figure 2b,c) was because of the removal of the biogas generated (consequently,  $CO_2$ ) from the system before  $H_2$  addition. As such, higher pH levels were observed in Exp3 whereby, the biogas contained higher amounts of  $CO_2$  before extraction. Similarly, when  $H_2$  was injected on Day 9 of in situ bimethanation with glucose, complete removal of  $CO_2$

caused pH to rise above 8.5 and up to 9.4, which was buffered with HCl (Wahid et al., 2019).

Higher pH levels measured in the test reactors of Exp2 and Exp3 compared to the corresponding controls demonstrate further  $CO_2$  removal from  $H_2/CO_2$  consumption further on from the  $H_2$  injection point. This effect was higher in the test of Exp3 than Exp2, thus, asserting a higher  $H_2/CO_2$  consumption in Exp3 than in Exp2. The change in pH between the test and control of Exp2 and Exp3 was between 0.1 and 0.3, which is similar to the 0.3 pH (8.0 to 8.3) increase reported during in situ bimethanation using manure (Luo et al., 2012). With further investigations, the addition of acidic whey to manure helped to buffer the system to maintain the pH below 8.0 (Luo & Angelidaki, 2013b). This agrees especially with Exp1, whereby, the pH was maintained below 8.0 throughout the AD period in the test due to a VFA-induced pH buffer.

Although FW is an acidic substrate, the pH buffering capacity of the liquid content reduced as the AD progressed because of the level of VFA available at the time of  $H_2$  addition.



**FIGURE 3** Sulphur profiles of the liquid content (dry basis) after  $H_2$  addition: (a) Exp1, (b) Exp2 and (c) Exp3. Shaded portion indicates the standard deviation from the mean



Therefore, besides from the feedstock, pH during in situ biomethanation can also be impacted by the digestion stage before the addition of H<sub>2</sub> as observed here.

### 3.3 | Competitive H<sub>2</sub> utilisation: sulphur degradation

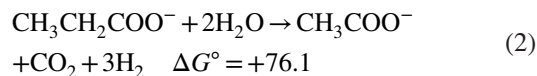
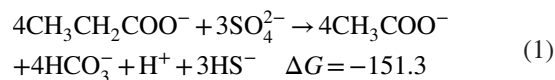
In the absence of oxygen, organic and inorganic sulphur can either be fermented or reduced to dissolved sulphides, which can be translated to the biogas as hydrogen sulphide and is principally progressed by the SRB (Peu et al., 2012). Moreover, sulphur can be distributed in different forms in a thermodynamic equilibrium during AD (Hao et al., 2014). This means its availability in any form will be dependent on the thermodynamic reaction and conditions of the system, such that an increase in one form will imply a decrease in the other. Hence, the potential for sulphide production becomes a function of sulphur biodegradation (Peu et al., 2012).

As presented in Figure 3a, regardless of the H<sub>2</sub> added to the test, sulphur degradation profiles in the control and test followed a similar pattern in Exp1. Because SRB would mainly metabolise intermediates from anaerobic fermentation/hydrolysis (Hao et al., 2014), they do not pose any competition during hydrolysis (Chen et al., 2008). As such, the early-stage reduction in the sulphur for both the control and test (up to Day 3) would follow the initial substrate solubilisation. Furthermore, a similar sulphur degradation trend observed in the test and control of Exp1 means that sulphur degradation was not particularly enhanced by the H<sub>2</sub> added, but followed a typical route as in the control without H<sub>2</sub> addition. This buttresses the assertion given in Section 3.1 that the H<sub>2</sub> added in the test of Exp1 was primarily utilised for CH<sub>4</sub> production.

The highest rate of sulphur degradation after H<sub>2</sub> addition was observed in the test of Exp2 (Figure 3b). Having already gone through initial solubilisation, the system at this stage was enriched with solubilised substrates, such as VFA, CO<sub>2</sub> and hydrolysed sulphur, thus, allowing competition for common substrates. Like Exp1, sulphur levels remained relatively unchanged in the control until Day15, while sulphur levels declined progressively in the test of Exp2 immediately after H<sub>2</sub> addition. Recall from Section 3.1 that H<sub>2</sub> added into the test of Exp2 was completely removed within 24 h. While this was not ultimately converted to biomethane, the decline in sulphur levels in the test for the same period suggests that the added H<sub>2</sub> was co-utilised for sulphur degradation.

Sulphur contents in the test of Exp2 continued to reduce even after the complete uptake of the added H<sub>2</sub>, indicating a progressive utilisation of other common substrates. The kinetics and thermodynamics during secondary

fermentation are in favour of SRB outcompeting the acetogens for common substrates (Chen et al., 2008) and the SRB-induced secondary fermentation reactions result in lower H<sub>2</sub> yields compared to the same progressed by acetogens. For instance, propionate degradation by SRB and typical acetogens (obligate hydrogen producers—OBHP) goes according to the reactions in Equations 1 and 2, respectively (Meng et al., 2013);



According to the above equations, SRB-induced propionate degradation (Equation 1) is more thermodynamically favourable but produces lower H<sub>2</sub> than OBHP-induced degradation (Equation 2). Therefore, VFA intermediates degradation by SRB could also have had an impact on the CH<sub>4</sub> yield by reducing the amount of H<sub>2</sub> released from such reactions, which would have been further utilised for CH<sub>4</sub> production. This supports the relatively lower CO<sub>2</sub> removal of 25.4% obtained in the test of Exp2, compared to 38.8% from the test of Exp1. As such, competition for common substrates including H<sub>2</sub> and VFA intermediates could have reduced the overall CO<sub>2</sub> removal potential for H<sub>2</sub> added in Exp2.

As there was a limited amount of solubilised substrate available at the time of adding H<sub>2</sub> to Exp3, competitive H<sub>2</sub> uptake was presumably limited. As a result, regardless of H<sub>2</sub> addition in the test, the sulphur levels of both the control and test in Exp3 remained relatively unchanged throughout the AD period (Figure 3c).

Overall, the percentage of sulphur degraded in both the control and test within each experiment was about the same. In Exp1, 93.5% and 94.1% sulphur removal was recorded from the control and test, respectively. Meanwhile, 100% sulphur removal was recorded in both control and test of Exp2 and Exp3 recorded the least sulphur degradation at 32.9% and 31.3% removal in the control and test, respectively. These results, showing similar levels of sulphur degradation in both the control and test, suggest that the addition of H<sub>2</sub> did not enhance the overall potential for sulphides production from FW. However, the competition for available substrates could potentially reduce H<sub>2</sub>/CO<sub>2</sub> conversion efficiencies to biomethane.

### 3.4 | Overall biogas upgrade

The biomethane and CO<sub>2</sub> yields from Exp1, Exp2 and Exp3 are presented in Figure 4. The addition of H<sub>2</sub> before VFA accumulation in the test of Exp1 enhanced biogas upgrade throughout the experiment (Figure 4a), thus, yielding lower

levels of  $\text{CO}_2$  throughout the experiment (Figure 4b). This would indicate that  $\text{H}_2$  produced from further VFA degradation was also utilised for biomethane production. In Exp2, AD progressed conventionally until Day 3 before  $\text{H}_2$  was added, higher competition for common substrates at this stage was believed to have reduced the potential increase in biomethane attainable from the  $\text{H}_2$  added. However, with the depletion of common solubilised substrates such as VFA within the system in Exp3, competition for  $\text{H}_2$  at this stage was probably limited, thus, allowing higher biomethanation than Exp2 for the  $\text{H}_2$  added.

In all three experiments, the addition of  $\text{H}_2$  improved the quality of the biogas, resulting in 12%, 4% and 10% biomethane increases in Exp1, Exp2 and Exp3, respectively. The ratio of  $\text{CO}_2$  reduction to biomethane increase in Exp1, Exp2 and Exp3 was 1.7, 0.8 and 1.5, respectively. This supports the foregoing discussions that  $\text{H}_2$  added in Exp2 was competed for and hence, not optimally utilised for biomethane production.

Figure 4c presents biogas composition from the entire process, such that, the data charts for Exp2 and Exp3 is inclusive of the biogas extracted before  $\text{H}_2$  addition. Therefore, although Exp3 had a higher  $\text{H}_2/\text{CO}_2$  conversion to biomethane

than Exp2 when the initial  $\text{CH}_4$  and  $\text{CO}_2$  yields generated before the addition of  $\text{H}_2$  in these experiments were added to the final yields, the biogas quality from Exp3 was the poorest (Figure 4c). This was due to a higher amount of  $\text{CO}_2$  accumulated by Day 6 compared to Day 3, at 386.8 and 193.4 ml, respectively. However, considering a higher biomethanation in Exp3, perhaps, biogas recirculation and continuous  $\text{H}_2$  addition might help to improve the overall quality of the biogas produced from such biomethanation set-up (Bassani et al., 2016, 2017; Burkhardt et al., 2015).

### 3.5 | The implication of the current study

Different  $\text{H}_2$  addition rates ranging from 0.3 to 40.2 L- $\text{H}_2$ /(L.day) have been used in in situ biomethanation studies at varying hydraulic retention times, achieving about 43.3%–100%  $\text{CO}_2$  removal (Agneessens et al., 2017; Alfaro et al., 2019; Bassani et al., 2016; Díaz et al., 2015; Luo & Angelidaki, 2012, 2013b; Mulat et al., 2017; Voelklein et al., 2019; Wahid et al., 2019; Wang et al., 2013). Most of these studies were conducted by injecting  $\text{H}_2$  some days after the AD had progressed; typically at a

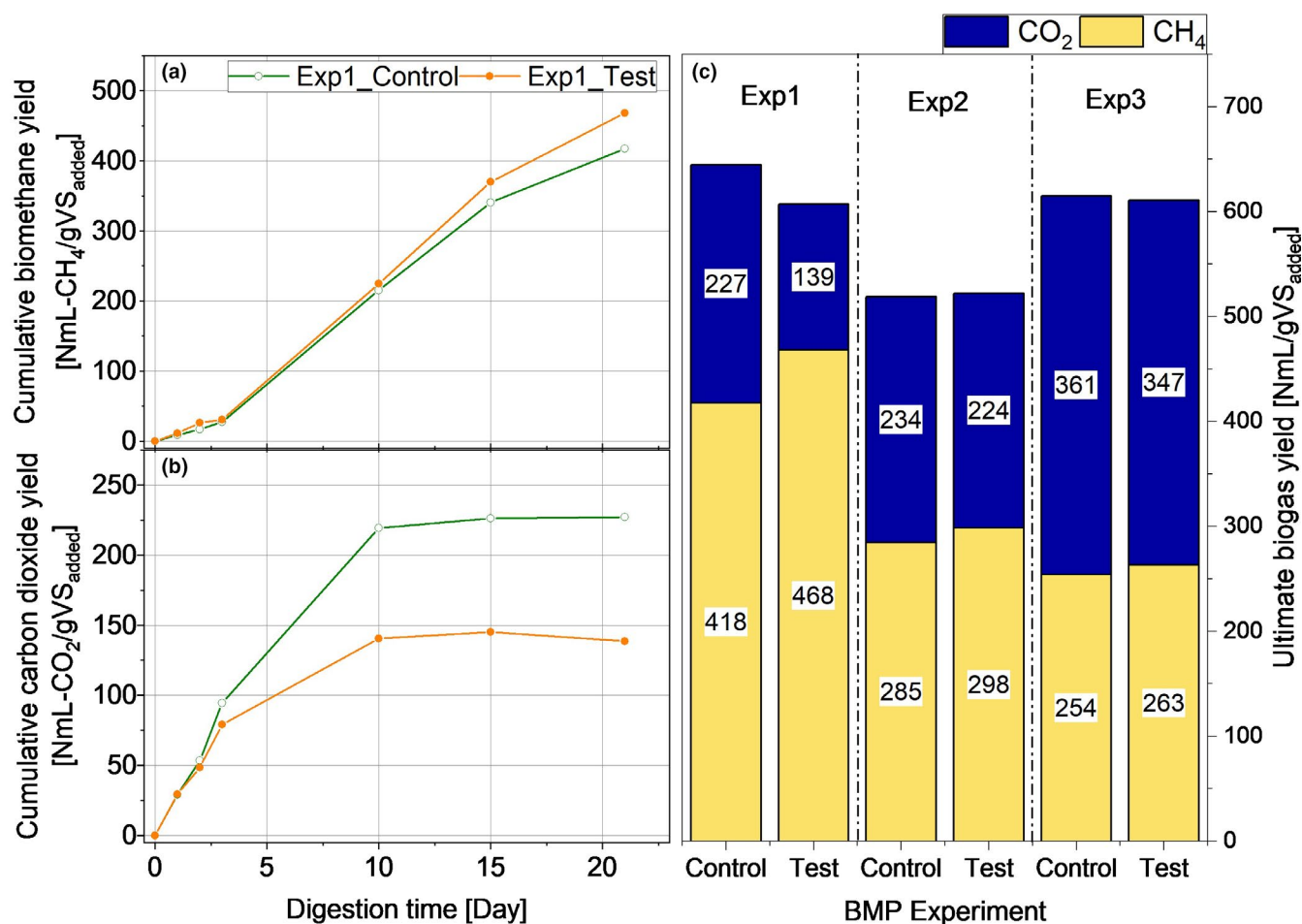
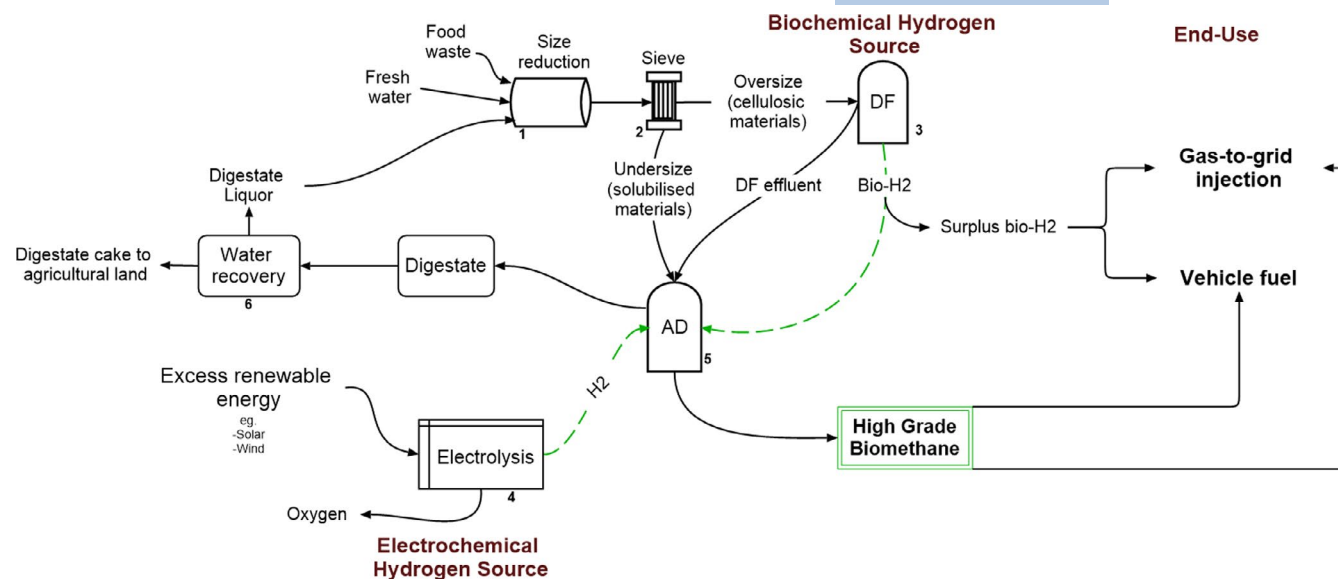


FIGURE 4 Cumulative methane (a) and carbon dioxide yield (b) from Exp1 and ultimate biogas yields (c) from Exp1, Exp2 and Exp3



**FIGURE 5** Schematic representation of the potential for integrating hydrogen production with anaerobic digestion of food waste for in-situ biomethanation: (1) Food waste grinding to reduce particle size; (2) Particle size fractionation to enhance solubility; (3) Biohydrogen production from oversize fractions characterised by cellulosic materials through dark fermentation (DF); (4) Hydrogen production by electrolysis using excess renewable energy; (5) Anaerobic digestion (AD) of solubilised food waste with the addition of hydrogen (insitu biomethanation) for high-grade biomethane production that could be injected into the gas grid or used as a vehicle fuel and (6) Opportunity for water recovery from the digestate to reduce system water demand and enhance a circular economy. The dash lines from steps 3 and 4 indicate alternative options for hydrogen production

steady state. However, the present study posits that the efficiency of  $H_2/CO_2$  conversion to biomethane is highest when  $H_2$  is added before the production/accumulation of VFA. Moreover, up to 8.1% of the potential biomethane yield was lost, when  $H_2$  was added during/after fermentation instead of at the start of the experiment.  $CO_2$  removal of up to 39% was achieved in the present study using  $H_2$  equivalent to 5% of the head-space at a 21-day hydraulic retention time. Therefore, for a 1 L reactor with an assumed 20% head-space, an equivalent of 10 ml- $H_2$ /L will be required, which is lower than the amounts used in previous studies.

In the UK, as of 31st January 2017, about 10 operational AD plants upgrade biogas to biomethane (by physicochemical methods) for injection into the gas grid; two of which are FW AD plants (WRAP, 2019). According to the present study, FW has huge potential as a sustainable resource for AD in the future, and in situ biomethanation could help to enhance its valorisation through GtG applications. However, before up-scaling for large (commercial) scale applications, it is important to optimise the added  $H_2$  ultimately for  $CO_2$  conversion to biomethane. This can be maximised by injecting  $H_2$  at the start of the AD set-up; in which case, start-up FW ADs would benefit the most.

Previous biomethanation studies suggest that  $H_2$  addition promotes the evolution of a more specialised microbial population of hydrogenotrophic methanogens (Bassani et al., 2017; Luo & Angelidaki, 2013b) and acclimatisation

to  $H_2$  by a continuous addition improved hydrogenotrophic methanogenesis (Treu et al., 2018). Therefore, it is proposed that for continuous in situ biomethanation,  $H_2$  addition should be done at the start-up phase of the reactor (where possible) and simultaneously with the FW loading. This should be followed by a stepwise increment in  $H_2$  loading at steady states, with the incorporation of digestate recycling to proliferate acclimatisation. This might allow for a lesser amount of  $H_2$  that can be obtained biologically by dark fermentation (Figure 5). A synergistic approach among renewable energy sources would be the best option for  $H_2$  production where possible.

That being the case, water electrolysis using excess renewable electricity, such as from solar (Figure 5), would give the purest and most consistent quantity of  $H_2$  for in situ biomethanation and have been proposed as an ideal  $H_2$  source for biomethanation (Angelidaki et al., 2018). However, these systems are not yet fully developed, therefore, for current (short term) practice, renewable biological  $H_2$  production by dark fermentation could be a more adaptable alternative. This can be easily incorporated since it requires similar technical knowhow as in the AD system.

To advance this study, future works will include a study of the microbial population during FW in situ biomethanation, as well as gradual increases in  $H_2$  loading to aid acclimatisation and efficient  $CO_2$  conversion to biomethane. Thus, producing a gas that can be fit for injection into the gas grid or for use as a transport fuel.

## 4 | CONCLUSIONS

The biological treatment of FW for renewable energy generation by AD can be coupled with H<sub>2</sub> injection. However, the injection point could impact the extent of H<sub>2</sub>/CO<sub>2</sub> conversion to biomethane and hence, should be carefully selected before setting up such systems. The addition of H<sub>2</sub> before the accumulation of VFA enhanced biomethanation throughout the AD period, resulting in the highest CO<sub>2</sub> conversion to biomethane. The addition of H<sub>2</sub> at the peak of VFA accumulation showed signs of possible propionate inhibition, especially if higher H<sub>2</sub> loads were applied. Also, increases in pH were observed when H<sub>2</sub> was added during and after fermentation. This study posits that different CO<sub>2</sub> conversion rates and biomethane yields can be achieved for the same amount of H<sub>2</sub> added during in situ biomethanation with FW. When H<sub>2</sub> was added before VFA accumulation, at the peak of VFA accumulation and depleted VFA intermediates, 39%, 25% and 34% of CO<sub>2</sub> were respectively removed. Correspondingly, 12%, 4% and 10% increases in biomethane yield were achieved. An enhanced competition for H<sub>2</sub> when added during fermentation is believed to have limited H<sub>2</sub>/CO<sub>2</sub> conversion to biomethanation. Hence, periods before accumulation and after degradation of VFA intermediates should be optimised for in situ biomethanation processes with FW. In general, biomethanation has a great potential to become the game-changer modification aimed at enhancing biological CO<sub>2</sub> capture and valorisation for the production of bio-based renewable energy from organic waste like FW.

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